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TITLE : POROUS HYDROPHILIC POLYOLEFIN FILM AND ITS PRODUCTION

ABSTRACT : PURPOSE: To impart hydrophilicity of excellent durability to a porous polyolefin film by selectively plasma-treating the surface part of the film to render it active and hydrophilic and treating the surfaces of the throughpores of the film with a hydrophilic agent.

CONSTITUTION: The surface part of a porous polyolefin film of a thickness of 1-25 μ m (desirably a high-MW polyethylene of an Mw of 1×10^6 - 15×10^6 and desirably of a throughpore diameter of 0.001-0.5 μ m) is plasma-treated in the presence of an oxygen-containing active gas or an inert gas such as nitrogen or argon to form an active layer of a wetting index ≥ 54 dyn/cm on the film. The plasma treatment is performed under conditions including a pressure of 10^{-2} - 10^1 Torr, a microwave power of 0.1-1kW, a treatment time of 1-100sec and their product of 2-40, desirably 4-20 in the case of an active gas, or a microwave power of 0.5-5kW, a treatment time of 10-1000sec and their product of 200-1000, desirably 250-800 in the case of an inert gas. The throughpores of this treated film are wetted with a hydrophilic organic solvent or treated with a surfactant solution to convert the film into a porous hydrophilic polyolefin film.

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⑭ 発 明 の 名 称

親水性ポリオレフィン多孔膜及びその製造方法

親水性ポリオレフィン多孔膜及びその製造方法

⑮ 特許請求の範囲

- ① 厚さ1〜2.5 μm のポリオレフィン多孔膜の表層部分としてプラズマ処理によるぬれ角が 45° 以上、及び(ア)その処理時間を1〜100秒としかつその積が(A)×(B)＝2〜40となるように表層部分をプラズマ処理し、該処理膜の貫通孔表面を有機溶剤蒸気処理するか、有機溶剤蒸気処理後に水置換するか、または界面活性剤溶液中で処理することを特徴とする親水性ポリオレフィン多孔膜の製造方法。
- ② 厚さ1〜2.5 μm のポリオレフィン多孔膜を、活性媒体の存在下に、A)マイクラ波出力が1〜100W、及び(B)その処理時間を1〜100秒としかつその積が(A)×(B)＝2〜40となるように表層部分をプラズマ処理し、該処理膜の貫通孔表面を有機溶剤蒸気処理するか、有機溶剤蒸気処理後に水置換するか、または界面活性剤溶液中で処理することを特徴とする親水性ポリオレフィン多孔膜の製造方法。

③ 厚さ1〜2.5 μm のポリオレフィン多孔膜を、活性媒体の存在下に、A)マイクラ波出力が1〜100W、及び(B)その処理時間を1〜100秒としかつその積が(A)×(B)＝2〜40となるように表層部分をプラズマ処理し、該処理膜の貫通孔表面を有機溶剤蒸気処理するか、有機溶剤蒸気処理後に水置換するか、または界面活性剤溶液中で処理することを特徴とする親水性ポリオレフィン多孔膜の製造方法。

⑯ 発明の詳細な説明

(産業上の利用分野)

本発明は、加工性に優れた親水性を有する、親水性ポリオレフィン多孔膜の材料及びその製造方法に関する。

(従来の技術)

ポリオレフィンの多孔膜は、機械的性質や化学的安定性に優れているため、各種の工業分野で利用が急速に広がっている。しかし、ポリオレフィンからなる多孔膜は、通常、加工性に劣る。

水に浸透に使用する場合には、親水化の処理が必要である。

従来、ポリオレフィン多孔膜の親水化法としては、(1)水と相溶性の良好なモノマー等の有機溶剤によつて膜の微細孔を湿潤処理した後、有機溶剤を水で置換する方法、(2)界面活性剤などの親水性物質を多孔膜の表面に吸着させる方法、(3)親水性モノマーを多孔膜に保持させた状態で放射線照射する方法、あるいは多孔膜に放射線を照射した後、親水性モノマーに接触させる方法(特開昭50-98565号公報、特開昭52-66564号公報、特開昭61-13664号公報、特開昭62-16373号公報)等が知られている。

しかしながら、(1)の有機溶剤湿潤・水置換方法は、膜の微細孔内の水が一旦抜けるとその部分は疎水性に戻り通水性が低下するため常に水を充ておくか、または度々親水化処理が必要である。また、(2)の物理的吸着方法は、長期間にわたつて使用すると親水性物質が離脱するた

(3)

と溶解性有機溶剤を湿潤処理もしくはその後の水置換または界面活性剤溶液等の親水化処理剤による処理とを組合せることにより、本発明の目的を達成することを見出し本発明を完成した。

すなわち、本発明の親水性ポリオレフィン多孔膜は、厚さ1~2.5 μm のポリオレフィン多孔膜の表面部分として、プラズマ処理によるぬれ増数が5.4 dyne/cm以上の活性化層を有し、かつ該多孔膜の貫通孔表面に、親水性有機溶剤もしくはその水溶液、水または界面活性剤を有してなることを特徴とする。

また、この親水性ポリオレフィン多孔膜の製造方法は、(1)厚さ1~2.5 μm のポリオレフィン多孔膜を、活性気体の存在下に、(A)マイクロ波出力が1~10W及び(1)その処理時間を1~10秒としかつその積が(A) \times (1)=2~40となるように表面部分をプラズマ処理し、次いで該処理後の貫通孔表面を、有機溶剤浸潤処理するか、有機溶剤湿潤処理後に水置換するか、または界面活性剤溶液で処理すること、及び(2)上

(5)

め必ずしも十分な親水化方法ではない。また、(3)の膜表面に化学的変性方法は、十分な重合と重合に必要な放射線照射により膜表面の微細孔に生ずる機械的強度の低下、また微細孔内部にモノマーの重合により膜内に変性するモノマー物質が離能に変化をきたして耐汚染性を失ひ、耐汚染性の消滅、さらには水中での膜の劣化を悪化により孔径を変化に生ずる微細孔の閉塞の問題が残されている。

(発明が解決しようとする課題)

本発明は、ポリオレフィン多孔膜の機械的性質、耐薬品性、分離性能を損うことなく、操作性に優れる親水性を付与したポリオレフィン多孔膜及びその製造方法の提供を目的とする。

(課題を解決するための手段)

本発明者らは、上記のような操作性に優れる親水性ポリオレフィン多孔膜について多種の検討を行った結果、ポリオレフィン多孔膜の表面部分のみを選択的にプラズマ処理して操作性を親水化する処理に高い効果の貫徹の表面を、

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親水性ポリオレフィン多孔膜の製造方法において、ポリオレフィン多孔膜を、不活性気体の存在下に(A)マイクロ波出力が1~10W及び(1)その処理時間を1~10秒としかつその積が(A) \times (1)=2~40となるように表面部分をプラズマ処理し、該処理後の貫通孔表面を有機溶剤浸潤処理するか、有機溶剤湿潤処理後に水置換するか、または界面活性剤溶液で処理することを特徴とするものである。

以下、本発明を詳細に説明する。

本発明において用いるポリオレフィン多孔膜は、エチレン、プロピレン、ヘキサエン、オクタエン、デカエン、ドデカエン、テトラメチルエチレン、1-ヘキサエン等を重合した結晶性の単独電合体または共電合体からなるものがある。これらのうち、エチレンを主体とする重量平均分子量が 5×10^4 以上、特に $1 \times 10^5 \sim 1.5 \times 10^6$ の範囲の超高分子量ポリエチレンからなるものが、分離性能・強度、かつ微細な貫通孔を有し空孔率の高い多孔膜を成形するうえから好ましい。

5

ポリオレフィン多孔膜は、例えば次のような方法で製造することが出来る。

（１）ポリオレフィン系（ α ）の重量多量、ポリオレフィン類のような不揮発性の溶媒中に加熱溶解して溶液を調製する。次に、このポリオレフィン溶液を適宜選択されるダイスからシート状に押出し、あるいは支持体上に流延し、その後、溶剤系または溶剤等でゲル化温度以下、好ましくは、 $5 \sim 20^\circ\text{C}$ の温度に冷却し、 $5 \sim 10$ 分の速度で冷却してゲル状シートを成形する。ゲル状シートの厚さは、通常 $0.1 \sim 5 \text{ mm}$ 程度に成形する。

次に、このゲル状シートを、温化メチレンのような易揮性溶媒に浸漬し溶媒を抽出して乾燥する方法、圧縮する方法、加熱する方法またはこれらの組合せによる方法等により脱溶媒処理する。ゲル状シート中の溶媒の除去量は、含まれる溶媒に対して少なくとも 1 の重量多量で、ゲル状シート中に含まれるポリオレフィンが、 α 系、 β 系、 γ 系、特に α 系と重量多量となるようにする。

(7)

は、膜の厚さ方向において表層部分（表裏）のみを選択的に活性化処理（処理層／未処理層／処理層）して親水化するために $1 \sim 2.5 \mu\text{m}$ の範囲であることが必要である。膜厚が $1 \mu\text{m}$ 未満では、活性化処理（一次処理ともいう）によって膜の破断強度が著しく低下し各種水処理用途の採用に耐えない。 $1 \sim 2.5 \mu\text{m}$ を越える場合は、一次処理において膜表面の親水性は得られるものの、活性化処理は不十分であり後の膜細胞表面を親水化剤により親水化処理を行った後の通水において、長期使用における膜腐蝕性が保たず通水性が徐々に低下する。

また、ポリオレフィン多孔膜の貫通孔径は、 $1 \sim 10 \mu\text{m}$ の範囲のものが好ましい。ポリオレフィン多孔膜の貫通孔径が極度に大きい場合は、プラズマ処理において貫通孔へのプラズマの進入頻度が高くなり、貫通孔内腔全層におきつつプラズマ処理されるために膜の厚さ方向において、表裏の表層部分のみを選択的に活性化処理することが難かしくなる。一方、貫

(9)

に脱溶媒処理することが容易で延伸する点から好ましい。

脱溶媒処理した膜を延伸するは、延伸方法に常のエンター法、ローラ法、注流法等によりこれらの方法の組合せによって規定の延伸率で延伸する。延伸温度は、ポリオレフィン系溶剤 $10 \sim 150^\circ\text{C}$ 以下で、好ましくは結晶分散温度、融点までの範囲である。又、延伸速度は、延伸方向に依りとも 1 倍以上、好ましくは $1 \sim 10$ 倍、面倍率で $1 \sim 10$ 倍以上、好ましくは $1 \sim 4$ 倍の倍が容易性、長強度及び縮短を貫通孔径の比率の倍を得るより多から好ましい。

得られた延伸成形物は、易揮性溶媒に浸漬して残留する溶媒を重量多量抽出するまで抽出除去した後、乾燥を容易して乾燥する。

このような、ポリオレフィン多孔膜の製造方法は、例えば特開昭 60-22473 号（特開昭 60-22473 号）及び特開昭 61-11366 号（特開昭 61-11366 号）に記載されているものである。

本発明におけるポリオレフィン多孔膜の厚さは、

(8)

通孔径が極度に小さい場合は、膜の乾燥後においても 1 atm 程度の乾燥気圧では乾燥速度が不十分となるため好ましくない。

本願発明におけるポリオレフィン多孔膜のプラズマ処理による一次処理は、発振放電、マイクロ放電等で、酸化性ガス、または酸化剤を注入したガスを脱出した活性気体の存在下、または窒素、アセトン、ヘリウム等の不活性気体の存在下で、前記のポリオレフィン多孔膜を接触させて行う。なお、不活性気体の存在下で処理した膜は、処理後に空気と接触させることにより活性化することが出来る。

処理条件は、電力が $10 \sim 100 \text{ W}$ 、 $10 \sim 100 \text{ W}$ 、(1) 活性気体の存在下では、 $1 \sim 10 \text{ W}$ 及び B 処理時間 $1 \sim 10$ 秒の範囲が好ましい。また、(2) 不活性気体の存在下では、 $1 \sim 10 \text{ W}$ 及び B 処理時間 $1 \sim 10$ 秒の範囲が好ましい。

(10)

好ましくは 0.50 ～ 0.80 の範囲で行う。処理条件が A・B が上記の範囲に満たない場合は、曝露面のぬれ指数が 5.4 (29.6%) 以上にならない曝露面の親水化が十分である。一方、上記範囲を超える場合は、次の親水化処理法での処理は表面の排水性を付与することより通水性を得るだけの親水化ができるが、曝露時の速度に低下や水中で膜が高度な膨張を起して細孔の孔径の拡大による物質の漏れが低下するという問題が生じる。

本発明のガラスマ処理によりポリオレフィン多孔膜の表面部分のみが活性化していることは、ガラスマ処理後の膜の断面を、例えばエントラキソングレート W などの染色材料で染色し、膜の表面部分の発色を光学顕微鏡で観察することによって確認することができる。これは、該ガラスマ処理によってポリオレフィン、多孔膜に生成するアミノ基やカルボキシル基とエントラキソングレート W との反応を利用して染色して発色させるものである。該ガラスマ処理にお

(13)

あげられる。これらの有機溶剤は、単一または二種以上の混合物、さらには水溶液で用いてもよい。上記の有機溶剤のうちでは、水と相溶性のよいメチルアルコール、エチルアルコール、n-ブタングリコール、グリセリン等のアルコール類が好ましく、特にエチルアルコールより重比重のものを好んで溶解が好ましい。

如界面活性剤吸着法としては、界面活性剤の溶解または混合液に膜を浸漬するか、あるいはこれらの液を膜に噴霧する方法があげられる。界面活性剤としては、カルガン酸塩、スルホオキシ酸塩、硫酸エステル塩、リン酸エステル塩、アオスフオン酸塩等の陰イオン性界面活性剤、アミン塩、第 4 級アンモニウム塩、コオスホニウム塩、スルホニウム塩等の陽イオン性界面活性剤、N,N'-ジメチル-N-エーテルキレート、カルボキシメチルアンモニウムイオン、N,N'-ジアルキルアミノアルキルカルボキ酸塩等により分子中に陰イオンと陽イオンとを含有する両イオン性界面活性剤、脂肪酸モノグ

(13)

いて、出力及び処理時間等の値 A・B が、本発明の範囲に満たない場合は、該ポリオレフィン多孔膜断面の表面部分に該溶剤による発色は認められないかまたは認められる。一方、出力及び処理時間とが、本発明の範囲を越える場合は、該ポリオレフィン多孔膜の断面の表面部分に該溶剤による発色が認められる。

次に、ガラスマ処理を施したポリオレフィン多孔膜は、その細孔の表面を、親水性を有するものもしくはその分解産物の処理法、すなわち水を浸水置換法または界面活性剤吸着法により、膜の貫通孔表面の親水化処理（浸水処理）を行う。

上記の親水性有機溶剤としては、水と相溶性による処理法、すなわち水を浸水置換法、または、水溶性の有機溶剤を膜内に細孔に溶解させておくか、または溶解させた後に、この有機溶剤を水で置換する方法があげられる。有機溶剤としては、アルコール類、ケトン類、エーテル類、エステル類、有機酸類、アミド系溶剤などの

(14)

リセリンエステル、脂肪酸モノアルキルエステル、脂肪酸ジアルキルエステル、脂肪酸トリアルキルエステル、脂肪酸アルカノールアミド、脂肪エチレングリコール縮合物等の非イオン性界面活性剤等をあげることができる。また、これらの界面活性剤は、塩酸とを併用してもよい。界面活性剤の濃度は、好ましくは、水相中に、1% 以下、より好ましくは、重比重以下であり、またはアルコール類等に溶解もしくは混合すること、この際、溶解性無機塩を併用してもよい。

上記の親水性有機溶剤もしくは水と相溶性の処理、すなわち水を浸水置換法または界面活性剤吸着法は、前記のガラスマ処理によりポリオレフィン多孔膜の表面部分の親水化に先づいて、膜の貫通孔表面を親水化して排水性を付与することができる。

以下に、本発明を実施例として詳細に説明する。なお、実施例における試験方法は次の通りである。

(1) 引張り破断強度: ASTM D 622

(14)

2. 親水化処理 (2.1.3.2)

(1) 親水化処理前の乾水透過速度

膜を平膜モジュールに組み込み、蒸留水がエタノール混合液（重量比 10/90）を透過させて親水化処理を行い、蒸留水で十分に洗浄した後、 3.0×10^{-2} の水圧をかけながら乾燥の透過量を測定して求めた。

(2) 親水化処理後の乾水透過速度

親水化処理（一次あるいは二次処理）膜を平膜モジュールに組み込み、蒸留水で十分に洗浄した後、 3.0×10^{-2} の水圧をかけながら乾燥の透過量を測定して求めた。

(3) 空気形乾燥後の乾水透過速度

親水化処理（一次及び二次処理）後の膜を水中に浸漬し、空気ポンプを用いて、時間空気形乾燥させた後、平膜モジュールに組み込み、蒸留水で十分に洗浄した後、 3.0×10^{-2} の水圧をかけながら乾燥の透過量を測定して求めた。

(15)

観察した。

参考例 1

重量平均分子量 (\overline{M}_w) が 2.5×10^5 のポリエチレン 4.0 重量%と流動パラフィン (6.4 cSt/4℃) 9.6 重量%との混合液 10.0 重量部に、2,6-ジ-tert-ブチル-4-メチルフェノール (TBC) 商品名—住友化学工業社製) 0.12 重量部とテトラキス[メチレン-(3-メタリ-ジ-tert-ブチル-4-ヒドロキシフェニル)]プロピオネート (メタン (ニルガノクタン 1.0) 商品名—チバガイギー社製) 0.2 重量部との酸化防止剤を加えて混合した。この混合液を増圧機付のオートクレーブに充填し、200℃で90分間増圧して均一な溶液を得た。

この溶液を加熱した金皿に充填し、15℃浴槽中で厚さ 4 mm のゲル状シートを成形した。

このゲル状シートを塩化メチレン 250 ml 中に 60 分間浸漬した後、平基板にはり付けた状態で塩化メチレンを蒸発乾燥し、流動パラフィ

(17)

3. 分子ふるい膜

上記 2、4 及び 5 に記載したポリマーを用いて、 3.0×10^{-2} の水圧下で、透過速度が 0.5 ml/min 未満の電圧、分子ふるい膜を製造及び使用する膜類の透過率を測定させたときに、乾燥中に含まれる溶媒の透過率を透過率が測定から求め、式 (1) により計算した。

膜類の阻止率 (1) = (乾燥中の溶媒透過率) / (中の溶媒透過率) (1)

分子分画曲線から阻止率 (2) を求めた。

4. プラズマ処理後の膜

エチレンオキシドモノマーを原料とし、重量%が酢酸と重量%を含む乾燥液中、プラズマ処理したポリエチレン多孔膜を製造し分間増圧した後、界面活性剤を含む水で洗浄した。得られたポリエチレン多孔膜を、光学顕微鏡下で観察し、図 1 に示す、特性の測定、観察結果、分子ふるい膜に相当するものを

(18)

ン含有量が 8.5 重量%の原液を作成した。

得られた原液シートを 9.0×10^{-2} の水圧で、軸延伸機にセットして、温度 15℃で、延伸速度 30 cm/min で、 3.0×10^{-2} の水圧に調整した状態で、得られた延伸膜を塩化メチレンで洗浄して残留する流動パラフィンを抽出除去した後、乾燥して、 3.0×10^{-2} の水圧で、 3.0×10^{-2} の超高分子量ポリエチレン多孔膜を得た。

得られたポリエチレン多孔膜の特性を表 1 に示した。

参考例 2

参考例 1 において、製造条件を若干変更し、以外は参考例 1 と同様にして、 3.0×10^{-2} の超高分子量ポリエチレン多孔膜を得た。

得られたポリエチレン多孔膜の特性を表 1 に示した。

(19)

表 1

番号	製 造 条 件				特 性				性 質			
	ゲル状 シート の厚さ (mm)	原料中の硫酸 パラフィン含 有量 (重量%)	延伸 倍率 縦×横 (倍)	延伸 温度 (℃)	膜 厚 (μm)	引張強度 1.5mm幅 (kg)	平均 孔径 (μm)	ぬれ 指数 (dyne/cm)	透水 速度 ($\frac{\text{cm}^3}{\text{cm}^2 \cdot \text{hr}}$)	一次処理後 透水 速度 ($\frac{\text{cm}^3}{\text{cm}^2 \cdot \text{hr}}$)	二次処理後 透水 速度 ($\frac{\text{cm}^3}{\text{cm}^2 \cdot \text{hr}}$)	分子量 ($\times 10^4$)
1	4	85.0	10×10	115	4	1.68	0.02	5.5	0	8.64	9.5	20
2	1	85.0	10×10	115	0.7	0.25	0.02	5.4	0	5.50		
3	6	85.0	5×5	115	28	5.2	1.12	5.4	0	3.80		
4	6	85.0	7×7	115	12	5.1	0.02	5.4	0	2.80		
5	10	85.0	7×7	122	16	5.4	1.02	5.5	0	4.50		

(19)

化処理の結果、

本発明のシリコンライン多孔膜は、ガラスや樹脂により形成された表面及び表面の表層部分のみを選択的に親水化する一次処理により親水指数が 4.55-5.00 以上を示す親水性を有する。さらに、その膜の細孔表面を溶解性有機溶剤または界面活性剤により親水化する二次処理により優れた通水性を有する。この膜の通水性は、膜の表層部分の選択的親水化により、膜の細孔部分に充填保持された水分または付着した界面活性剤が、空気との接触においても容易に離脱または分解されないため、耐久性にも優れた通水性を有する。

また、膜の表層部分の選択的な親水化は、膜の機械的強度を低下させることなく、さらには膜形成中において高度に整列を促して貫通孔の孔径が均一で、物質分離性能が低下するところもない。

以上、本発明のシリコンライン多孔膜は、強度、親水性および耐久性及び分離性に優れ

たものであること、各種の用途に好適に利用して有用である。

例 1	4	0.1	0.1
例 2	4	0.1	0.1
例 3	4	0.1	0.1
例 4	4	0.1	0.1

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HYDROPHILIC POLYOLEFIN POROUS FILM

AND METHOD OF MANUFACTURE THEREOF

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1. Title of the Invention: HYDROPHILIC POLYOLEFIN POROUS FILM
AND METHOD OF MANUFACTURE THEREOF

2. Claims

1. A hydrophilic polyolefin porous film, characterized by the fact that an activated layer with a wetting index of 54 dyne/cm or more of a plasma treatment is provided as a surface layer part of a polyolefin porous film with a thickness of 1-25 μm ; and a hydrophilic organic solvent or its aqueous solution, water, or surfactant are provided to the surfaces of through holes of said porous film.

2. A method for manufacturing a hydrophilic polyolefin porous film, characterized by the fact that the surface layer part of a polyolefin porous film with a thickness of 1-25 μm is plasma-treated in the presence of an active gas under the conditions of (A) a microwave output of 0.1-1 KW, (B) a treatment time of 1-100 sec, and its product (A) x (B) of 2-40; and the through hole surface of said film treated is wet-treated with an organic solvent or substituted by water after wet-treating with an organic solvent or treated with a surfactant solution.

* Numbers in the margin indicate pagination in the foreign text.

3. A method for manufacturing a hydrophilic polyolefin porous film, characterized by the fact that the surface layer part of a polyolefin porous film with a thickness of 1-25 μm is plasma-treated in the presence of an inert gas under the conditions of (A) a microwave output of 0.5-5 KW, (B) a treatment time of 10-1,000 sec, and its product (A) x (B) of 200-1,000; and the through hole surface of said film treated is wet-treated with an organic solvent or substituted by water after wet-treating with an organic solvent or treated with a surfactant solution.

3. Detailed explanation of the invention

(Industrial application field)

The present invention pertains to a hydrophilic polyolefin porous film with excellent durability to which a hydrophilicity is given, and its manufacturing method.

(Prior art)

Since the polyolefin porous film has excellent mechanical properties and chemical resistance, its application is rapidly broadened in various kinds of fields. However, since the porous film composed of polyolefin is hydrophobic, if it is used in water treatment, etc., a hydrophilic treatment is required. /2

As conventional hydrophilic methods of the polyolefin porous film, (1) a method that wet-treats pores of the film with an organic solvent such as alcohol with good compatibility with water and substitutes the organic solvent by water, (2) a method that adsorbs a hydrophilic substance such as surfactant to the

surface of the porous film, (3) a method that irradiates the porous film with a radiation in a state in which a hydrophilic monomer is held or a method that irradiates the porous film with a radiation and contacts it with a hydrophilic monomer (Japanese Kokai Patent Application Nos. Sho 50[1975]-98568, Sho 59[1984]-160504, Sho 61[1986]-106640, and Sho 62[1987]-163703), etc., are known.

However, In the organic solvent-wetting/water-substituting method (1), once the water in the pores of the film is discharged, since the part is returned to the hydrophobicity and the water permeability is lowered, it is necessary to always fill the part with water or to be re-subjected to a hydrophilic treatment. Also, in the physical adsorption method (2), if the film is used over a long term, since the hydrophilic substance is separated, the method is not necessarily a sufficient hydrophilic method. Furthermore, in the chemical modifying method of the film surface of (3), since the mechanical strength is decreased by the degradation of the film material due to the radiation irradiation required for a sufficient graft polymerization and the porous surface state is extremely changed by the polymer of the monomer, the substance separability is changed, so that the clogging resistance or stain resistance are lost. Furthermore, the separability is lowered by the change of the hole diameter due to a high swelling of the film in water.

(Problems to be solved by the invention)

The purpose of the present invention is to provide a

polyolefin porous film with good durability, to which a hydrophilicity is given without damaging the mechanical properties, chemical resistance, and separability of the polyolefin porous film, and its manufacturing method.

(Means to solve the problems)

These inventors variously reviewed the above-mentioned hydrophilic polyolefin porous film with excellent durability. As a result, it was discovered that the purpose of the present invention was achieved by combining an activating and hydrophilic treatment of only the surface layer part of the polyolefin porous film through a selective plasma treatment with a water-soluble organic solvent wet-treatment or a treatment of a water substitution or hydrophilic treating agent such as surfactant solution.

In other words, the hydrophilic polyolefin porous film of the present invention is characterized by the fact that an activated layer with a wetting index of 54 dyne/cm or more of a plasma treatment is provided as a surface layer part of a polyolefin porous film with a thickness of 1-25 μm ; and a hydrophilic organic solvent or its aqueous solution, water, or surfactant are provided to the surfaces of through holes of said porous film.

Also, (1) the method for manufacturing the hydrophilic polyolefin porous film is characterized by the fact that the surface layer part of the polyolefin porous film with a thickness of 1-25 μm is plasma-treated in the presence of an active gas

under the conditions of (A) a microwave output of 0.1-1 KW, (B) a treatment time of 1-100 sec, and its product (A) x (B) of 2-40; and the through hole surface of said film treated is wet-treated with an organic solvent or substituted by water after wet-treating with an organic solvent or treated with a surfactant solution. Also, (2) the method for manufacturing the above-mentioned hydrophilic polyolefin porous film is characterized by the fact that the surface layer part of the polyolefin porous film is plasma-treated in the presence of an inert gas under the conditions of (A) a microwave output of 0.5-5 KW, (B) a treatment time of 10-1,000 sec, and its product (A) x (B) of 200-1,000; and the through hole surface of said film treated is wet-treated with an organic solvent or substituted by water after wet-treating with an organic solvent or treated with a surfactant solution.

Next, the present invention is explained in detail.

As the polyolefin porous film being used in the present invention, a crystalline homopolymer or copolymer in which ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, etc., are polymerized is mentioned. Among them, a superhigh-molecular polyethylene mainly composed of ethylene with a weight average molecular weight of 5×10^5 or more, especially 1×10^6 - 15×10^6 is preferable in molding a porous film with high elastic modulus, high strength, and fine through holes at high porosity.

The polyolefin porous film can be manufactured as follows, /3
for instance.

1-10 wt% of the above-mentioned polyolefin is heated and

dissolved in a nonvolatile solvent such as paraffin oil, so that a solution is prepared. Next, the polyolefin solution is extruded in a sheet shape from a die being appropriately selected or extended on a support and cooled to a gelation temperature or lower, preferably a temperature of 15-20°C at a rate of at least 50°C/min in a water bath, air bath, or solvent, so that a gel-state sheet is molded. The thickness of the gel-state sheet is usually molded at about 0.1-5 mm.

Next, the solvent is removed from the gel-state sheet by a method that extracts the solvent by dipping into an easily volatile solvent such as methylene chloride and dries it, a heating method, or a combined method of these methods. The amount of solvent being removed from the gel-state sheet is at least 10 wt% relative to the solvent being included, and the solvent removal treatment in which the polyolefin being included in the gel-state sheet is 10-90 wt%, especially 10-60 wt% is preferable in terms of stretch at a high magnitude.

The gel-state sheet after removing the solvent is heated and biaxially stretched at a prescribed magnitude by an ordinary tenter method, a roll method, a drawing method, or a combination of these methods. The stretch temperature is the melting point of the polyolefin + 10°C or lower, preferably in a range from the crystal dispersion temperature to the melting point. Also, the stretch magnitude is at least twice or more, preferably 5-20 times in a uniaxial direction and 10 times or more, preferably 25-400 times at a face magnitude in terms of acquisition of a

film with a high elasticity, a high strength, and a large porosity of fine through holes.

For the stretched molded product obtained, the remaining solvent is extracted and removed until less than 1 wt% by dipping into an easily volatile solvent, and after evaporating the solvent is evaporated, the molded product is dried.

Such a method for manufacturing the polyolefin porous film is presented in Japanese Kokai Patent Application Nos. Sho 60[1985]-242035 and Sho 61[1986]-106640.

It is necessary for the thickness of the polyolefin porous film in the present invention to be in a range of 1-25 μm to make only the surface layer part (surface and back face) hydrophilic in the thickness direction of the film by selectively applying an activation treatment (treating layer/untreating layer/treating layer). If the film thickness is less than 1 μm , the rupture strength of the film is considerably decreased by the activation treatment (also called a primary treatment), so that the film cannot withstand various kinds of water treatment purposes. On the other hand, if the film thickness exceeds 25 μm , although the hydrophilicity of the film surface can be obtained in the primary treatment, the activation treatment is insufficient, and in the water permeation after the hydrophilic treatment of the porous surface of the film by a hydrophilic agent, the wet state cannot be maintained in the use over a long term, and the water permeability is slowly lowered.

Also, the through hole diameter of the polyolefin porous

film is preferably in a range of 0.001-0.5 μm . If the through hole diameter of the polyolefin porous film is extremely large, the advance frequency of the plasma into the through holes is raised in said plasma treatment, so that the entire layer in the through holes is plasma-treated. Thereby, it is difficult to selectively apply the activation treatment to only the surface layer part of the surface and back face at the thickness side of the film. On the other hand, if the through hole diameter is extremely small, the water permeation rate is insufficient at a low operation pressure of about 1 atm, even after the hydrophilic treatment, which is not preferable.

The primary treatment of the plasma treatment of the polyolefin porous film in the present invention is carried out by contacting the above-mentioned polyolefin porous film in the presence of an oxidizing gas such as an active gas in which oxygen or a mixed gas of oxygen and nitrogen, air, argon, helium, etc., is excited or in the presence of an inert gas such as nitrogen, argon, and helium by high-frequency discharge, microwave discharge, etc. Also, the film treated in the presence of the inert gas can be activated by contacting with the air after treating.

As the treatment conditions, the pressure is 10^{-2} - 10^1 torr, and (1) in the presence of the active gas, the product of a microwave output (A) of 0.1-1 KW and a treatment time (B) of 1-100 sec is in a range of $(A) \times (B) = 2-40$, preferably 4-20. Also, (2) in the presence of the inert gas, the product of a

microwave output (A) of 0.5-5 KW and a treatment time (B) of 10-1,000 sec is in a range of $(A) \times (B) = 200-1,000$, preferably 250-800. If $(A) \times (B)$ of the treatment conditions does not meet the above-mentioned range, the wetting index of the film surface does not reach 54 dyne/cm or more, and the hydrophilicity of the film surface is insufficient. On the other hand, if the treatment conditions exceed the above-mentioned range, though the hydrophilicity for only obtaining a water permeability can be realized without obtaining the hydrophilicity of the porous part surface in the next hydrophilic treating agent, the mechanical strength of the film is decreased, and the film is highly swollen in water, so that the substance separability due to the expansion of the hole diameter of the pores is lowered.

The activation of only the surface layer part of the polyolefin porous film by the plasma treatment of the present invention can be confirmed by observing the color generation of the surface layer part of the film by an optical microscope after dyeing the cross section of the film after the plasma treatment with a dye material such as anthraquinone blue SWF. The color is generated by dyeing using the reaction of the amino group and the carboxyl group being generated in the polyolefin porous film by said plasma treatment and the anthraquinone blue SWF. In said plasma treatment, if the product $(A) \times (B)$ of the output (A) and the treatment time (B) does not meet the range of the present invention, the color generation due said dyeing cannot be recognized or insufficient in the surface layer part of the cross

section of said polyolefin porous film. On the other hand, if the output (A) x the treatment time (B) exceeds the range of the present invention, the color generation due to said dyeing is recognized in the entire layer of the cross section of said polyolefin porous film.

Next, in the polyolefin porous film after the plasma treatment, its porous part surface is subjected to a hydrophilic treatment (also called a secondary treatment) of the through hole surface of the film by (a) a treatment method using a hydrophilic organic solvent or its aqueous solution, (b) an organic solvent wetting/water substitution method, or (c) a surfactant adsorption method.

As the above-mentioned treatment method using a hydrophilic organic solvent or its aqueous solution (a) and the organic solvent wetting/water substitution method (b), a method that impregnates the pores in the film with a water-soluble organic solvent or impregnates the pores with an organic solvent and substitutes the organic solvent by water is mentioned. As the organic solvent, alcohols, ketones, esters, ethers, organic acids, amide group solvents, etc., are mentioned. These organic solvents may be used alone or as a mixture of two kinds or more or as an aqueous solution. Among the above-mentioned organic solvents, alcohols such as methyl alcohol, ethyl alcohol, ethylene glycol, and glycerin having good compatibility with water are preferable, and in particular, an aqueous solution containing 50 wt% or more ethyl alcohol is preferable.

As the surfactant adsorption method (c), the film is dipped into a surfactant solution or a mixed solution, or these solutions are sprayed on the film. As the surfactant, anionic surfactants such as carboxylate, sulfonate, sulfuric ester, phosphoric ester, and phosphonate, cationic surfactants such as amine salt, quaternary ammonium salt, phosphonium salt, and sulfonium salt, amphoteric surfactants containing anions and cations such as N,N-dimethyl-N-alkyl-N-carboxymethyl ammonium betaine, and N,N-dialkyl aminoalkylene carboxylate, nonionic surfactants such as fatty monoglycerin ester, fatty polyglycol ester, fatty sorbitan ester, fatty sucrose ester, fatty alcohol amide, and polyethylene glycol condensate can be mentioned. Also, these surfactants may be used in combination of two kinds or more. The concentration of the surfactants is preferably 0.1 wt% or more, more preferably 1 wt% or more and is dissolved or mixed in water or alcohols. At that time, a deliquescent inorganic salt may also be combined.

In the above-mentioned treatment (a) using a hydrophilic organic solvent or its aqueous solution, organic solvent wetting/water substitution method (b), or surfactant adsorption method (c), the water permeability can be rendered by making the through hole surface of the film hydrophilic in addition to the hydrophilicity of the surface layer part of the polyolefin porous film by the above-mentioned plasma treatment.

Next, the present invention is explained in detail by application examples. Also, testing methods in the application

examples are as follows.

(1) Tensile rupture strength: ASTM D 882

(2) Wetting index: JIS K 6768

/5

(3) Pure water permeation rate before a hydrophilic treatment:

The film was assembled into a flat film module, subjected to a hydrophilic treatment by permeating a mixed solution of distilled water/ethanol (a volume ratio of 50/50) into it, and sufficiently washed with distilled water. Then, when a water pressure of 380 mmHg was applied to it, the amount of filtrate permeated was measured.

(4) Pure water permeation rate after the hydrophilic treatment

(primary or secondary treatment): The hydrophilic-treated

(primary or secondary treatment) film was assembled into the flat film module and sufficiently washed with distilled water, and when a water pressure of 380 mmHg was applied to it, the amount of filtrate permeated was measured.

(5) Pure water permeation rate after contacting with the air: The

film after the hydrophilic treatment (primary or secondary treatment) was dipped into water, contacted with the air for 1 h by an air pump, and sufficiently washed with distilled water, and when a water pressure of 380 mmHg was applied to it, the amount of filtrate permeated was measured.

(6) Fractionated molecular weight: Using the module described in the above-mentioned (3), (4), and (5), when an aqueous solution of 0.05 wt% Pullulan (made by Showa Denko K.K., saccharides with a molecular weight of 100,000, 186,000, and 380,000) was

circulated at a differential pressure of 380 mmHg, the concentration of the Pullulan being included in the filtrate was attained from the measurement of the differential refractive index and calculated by the following equation.

$$\text{Inhibition rate of saccharides} = \{1 - (\text{Pullulan concentration in the filtrate} / \text{Pullulan concentration in the raw solution})\} \times 100$$

The molecular weight showing the inhibition rate of 90% was attained from a molecular fractionation curve.

(7) Dyeing of plasma-treated part: The plasma-treated polyolefin porous film was dipped into an aqueous solution containing 0.2 wt% anthraquinone blue SWF and 0.2 wt% acetic acid, boiled for 5 min, and washed with water containing a surfactant. For the polyolefin porous film obtained, it was observed by a microscope (x 1,500 times) that the activated part (hydrophilic part) was deeply dyed.

Referential Example 1

An antioxidant of 2,6-di-t-butyl-p-cresol ("BHT": trade name, made by Sumitomo Chemical Co., Ltd.) at 0.125 part by weight and tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate]methane ("Irganox 1010": trade name, made by Chiba Gaigisha) at 0.25 part by weight was added to a mixed solution of 40 wt% polyethylene with a weight average molecular weight ($M_w(\text{bar})$) of 2×10^5 and 96.0 wt% flow paraffin (64 cst/40°C. at 100 parts by weight and mixed. The mixed solution was filled into an autoclave with a stirrer and stirred at 200°C for 90 min,

so that a uniform solution was obtained.

The solution was filled into a heated mold and rapidly cooled to 15°C, so that a gel-state sheet with a thickness of 4 mm was molded.

The gel-state sheet was dipped for 60 min into 250 ml methylene chloride and attached to a smooth plate, and in this state, the sheet was dried by evaporating the methylene chloride, so that an original sheet with a flow paraffin content of 85.0 wt% was prepared.

The original sheet obtained was cut into 9 x 9 cm, set to a biaxial stretcher, and simultaneously biaxially stretched at a temperature of 115°C, a stretch rate of 30 cm/min, and 10 x 10 times. The stretched film obtained was washed with methylene chloride, and after extracting and removing the residual flow paraffin, the film was dried and thermally set at 120°C, so that a superhigh-molecular polyethylene porous film with a thickness of 4 μm was obtained.

The characteristics of the polyethylene porous film obtained were shown in Table I.

Referential Examples 2-5

Similarly to Referential Example 1 except for setting the manufacture conditions as shown in Table I in Referential Example 1, superhigh-molecular polyethylene porous films were respectively obtained.

The characteristics of the polyethylene porous films obtained were shown in Table I.

Table I

/6

表 1

3.

2.

1.

1. 参考例 No	2. 製造条件						3. 特性					4. 空気乾燥後	
	4. ゲル状 シート の厚さ (mm)	5. 反応中の流動 パラフィン含 有量 (重量%)	6. 延伸 比率 縦×横 (倍)	7. 延伸 温度 (℃)	8. 厚 膜 (μm)	9. 引張破断 強度 15mm幅 (kg)	10. 平均 孔径 (μm)	11. ぬれ 指数 (dyne/cm)	12. 透水 速度 (L/m ² hr. atm)	13. 二次処理後 透水 速度 (L/m ² hr. atm)	分画 分子重 60,000 (10 ⁴)	透水 速度 (L/m ² hr. atm)	分画 分子重 180,000 (10 ⁴)
1	4	85.0	10×10	115	4	1.68	0.02	33	0	8.64	24	8.5	20
2	1	85.0	10×10	115	0.7	0.25	0.02	34	0	3250	27	—	—
3	6	85.0	5×5	115	28	52	0.02	34	0	380	25	—	—
4	6	85.0	7×7	115	12	51	0.02	34	0	780	25	—	—
5	10	85.0	7×7	122	16	54	0.02	35	0	430	26	—	—

1. Referential Example No.
2. Manufacture conditions
3. Characteristics
4. Thickness of gel-state sheet (mm)
5. Flow paraffin content of original plate (wt%)
6. Stretch magnitude, vertical x horizontal (times)
7. Stretch temperature ($^{\circ}\text{C}$)
8. Film thickness (μm)
9. Tensile rupture strength, 15 mm in width (kg)
10. Average hole diameter (μm)
11. Wetting index (dyne/cm)
12. Water permeation rate ($\text{l/m}^2\text{h}\cdot\text{atm}$)
13. After secondary treatment
14. After air contact
15. Water permeation rate ($\text{l/m}^2\text{h}\cdot\text{atm}$)
16. Fractionated molecular weight (10^4)
17. Water permeation rate ($\text{l/m}^2\text{h}\cdot\text{atm}$)
18. Fractionated molecular weight ($\times 10^4$)

Application Example 1

/7

The polyethylene porous film of Referential Example 1 was washed with hexane, dried, and treated at a pressure of 1 torr and an output of 0.3 KW for 30 sec in an air atmosphere by a microwave plasma treatment apparatus (made by Toshiba

Corporation, TMZ-2032 type). The tensile rupture strength, the wetting index, the water permeation rate, and the fractionated molecular weight of the film were shown in Table II. Also, in dyeing of the cross section of the treated film with an aqueous solution of anthraquinone blue SWF, a color generation was seen in the surface layer part of the film cross section.

Next, the film was dipped into an aqueous solution of 50 wt% ethyl alcohol and washed with water. The water permeation rate and the fractionated molecular weight of the film were also described in Table II.

Furthermore, after contacting the film with the air in water, the water permeation rate and the fractionated molecular weight were also described in Table II.

Application Examples 2-4 and Comparative Examples 1-4

Similarly to Application Example 1 except for adopting the conditions shown in Table II for the microwave plasma treatment in Application Example 1, a treatment was carried out. In dyeing of the cross sections of each treated film with an aqueous solution of anthraquinone blue SWF, a color generation was seen in the surface layer parts of the film cross sections in Application Examples 2-4, however in Comparative Example 1 and 3, the color generation of the surface layer parts was insufficient. In Comparative Examples 2 and 4, the color generation was seen in the entire layers of the film cross sections.

The characteristics of the films obtained were also described in Table II.

Application Example 5

Similarly to Application Example 1 except for dipping the film after the microwave plasma treatment into an aqueous solution of 1 wt% soda alkyl naphthalenesulfonate of an anionic surfactant (Pellex NB Paste, made by Kao Soap K.K.) for 10 sec and drying it with the air in Application Example 1, a treatment was carried out. The characteristics of the film obtained were also described in Table II.

Comparative Example 5

The polyethylene porous film of Referential Example 2 was subjected to a microwave plasma treatment similarly to Application Example 1, so that a hydrophilic polyolefin porous film was obtained. However, the film was broken at a water pressure of 380 mmH₂O.

Comparative Example 6

The polyethylene porous film of Referential Example 3 was treated similarly to Application Example 2. The characteristics of the film obtained were also described in Table II.

Application Examples 6 and 7

Similarly to Application Example 1 except for using the polyethylene porous films of Referential Example 4 (for Application Example 6) and Referential Example 5 (for Application Example 7) and applying the microwave plasma treatment under the conditions shown in Table II, a treatment was carried out. In dyeing of the cross sections of each treated film with an aqueous solution of anthraquinone blue SWF, a color generation was seen

in the surface layer parts of the film cross sections.

The characteristics of the films obtained were also described in Table II.

Application Example 8

Similarly to Application Example 1 except for dipping the film after the microwave plasma treatment into an aqueous solution of 50 wt% ethyl alcohol and not washing it with water in Application Example 1, the water permeation rate and the fractionated molecular weight were attained. The characteristics of the films obtained were also described in Table II.

Application Example 9

Similarly to Application Example 1 except for dipping the film after the microwave plasma treatment into a pure ethyl alcohol and not washing it with water in Application Example 1, the water permeation rate and the fractionated molecular weight were attained. The characteristics of the films obtained were also described in Table II.

Table II

/6

1.	2. 物理条件				3. 特				12 時		13 時	
	4. 圧力 (torr)	5. マイクロ波出力 (W)	6. 照射時間 (分)	7. 雰囲気	8. 引張器 強度 (kg/cm ²)	9. 分子速度 係数 ($\times 10^3$)	10. 透過率 (%)	11. 分子速度 係数 ($\times 10^3$)	12 時 透過率 (%)	13 時 透過率 (%)	12 時 分子速度 係数 ($\times 10^3$)	13 時 分子速度 係数 ($\times 10^3$)
実験例	1	0.5	30	7.	9	162	54	23	875	24	827	24
2	1	0.5	60	20.	18	145	54	24	904	25	921	24
3	1	1.0	270	21.	270	153	54	23	840	23	934	23
4	1	1.0	540	21.	540	140	54	24	915	25	908	24
5	1	0.5	30	20.	9	162	54	23	887	24	825	24
6	1	0.5	400	20.	25	393	54	26	862	27	769	25
7	1	1	300	21.	900	435	54	24	454	25	495	24
8	1	0.5	30	20.	9	162	54	23	850	24	815	24
9	1	0.5	30	20.	9	162	54	23	825	25	808	23
比較例	1	0.5	5	20.	15	154	31	0	825	23	120	18
2	1	1.0	90	20.	90	180	54	240	820	240	2010	140
3	1	0.5	480	21.	164	150	34	0	255	25	213	21
4	1	1.0	1080	21.	1080	110	54	222	1810	240	1540	240
5	1	0.5	30	20.	9	162	54	23	825	25	808	23
6	1	0.5	30	20.	15	154	31	0	825	23	120	18

A-22.

KEY TO TABLE II.

1. Example
2. Treatment conditions
3. Characteristics
4. Pressure (torr)
5. (A) Microwave output (KW)
6. (B) Irradiation time (sec)
7. Atmosphere
8. Tensile rupture strength (kg/15 mm in width)
9. Wetting index (dyne/cm)
10. Water permeation rate (l/m²h·atm)
11. Fractionated molecular weight ($\times 10^4$)
12. After secondary treatment
13. After air contact
14. Water permeation rate (l/m²h·atm)
15. Fractionated molecular weight ($\times 10^4$)
16. Water permeation rate (l/m²h·atm)
17. Fractionated molecular weight ($\times 10^4$)
18. Application Example 1
19. Comparative Example 1
20. Air
21. Nitrogen
22. Film breakage

The polyolefin porous film of the present invention exhibits a hydrophilicity with a wetting index of 54 dyne/cm or more by the primary treatment for selectively activating only the surface layer part of the surface and the back face of the film by a plasma treatment. Furthermore, the film exhibits an excellent water permeability by the secondary treatment for making the porous surface of the film hydrophilic with a water-soluble organic solvent or surfactant. As for the water permeability of the film, with the selective hydrophilicity of the surface layer part of the film, since the moisture substituted and held in the porous part of the film or the surfactant attached is not easily separated or peeled off by the contact with the air, the film has a water permeability with excellent durability.

Also, the selective hydrophilicity of the surface layer part of the film does not decrease the mechanical strength of the film, and since the film is highly swollen in water, the diameter of the through holes is expanded, so that the substance separability is not lowered.

Thus, since the polyolefin porous film of the present invention is excellent in strength, hydrophilicity and its durability, and separability, it is useful for various kinds of water treatment fields.